

## Chapter 1

### Research background

#### 1.1. Introduction

Since last decade main concern was focused on the traditional wood preservatives that are presently used to improve durability of wood. Numbers of scientific research reports have been revealed that typical preservatives that contain toxic chemical bases; for example arsenic, zinc, copper, chromium or oil base chemicals; e.g. creosote, etc. are problematic for the environment. Reports indicate that creosote is carcinogenic (Karlehagen, 1990), arsenic leaches out of the treated wood and pollutes soils and waters (Bergholm, 1990; Garcia & Rowland, 2001; Solo-Gabriele *et al.*, 1998, 1999, 2000, 2002; Townsend *et al.*, 2001a,b&c, 2001; Hauserman, 2002a,b&c; DeWitt, 2002a&b; Gainesville Sun Newspaper, 2002a&b). Disposing the waste CCA treated wood in fire furnace also is not a right solution due to high ash content remaining after furnacing (Solo-Gabriele *et al.*, 2002; Cooper, 1990). Chromium is also toxic and produces dermal inhalation diseases (Chen *et al.*, 2000). It leaches out due to rainfall (Solo-Gabriele *et al.*, 2002). Due to high pressure (public, media and law) against using toxic based preservatives, the use of these preservatives are being subjected to decrease because of their environmental impacts or some of them (for example CCA) are going to be banned in Europe (Germany and The Netherlands) and USA (Schert, 2002; EPA report, 2002) and Canada (PMRA report, 2002).

Considerable improvements have been made in formulation and fixation of traditional preservatives to prevent their leaching into environment, soil or water. However, there is still no real solution.

Wood modification is new approach to preserve wood from biological and climatological damages with environmental friendly chemicals. In wood modification the basic chemistry of cell wall polymers is altered which can change important properties of wood including durability, dimensional stability, hardness and UV-stability. Controlling the moisture content in wood is a very effective way to protect it from physical damages or some biological attack, especially fungal attack.

#### 1.2. Chemical wood modification

Most of the researches in the field of chemical modification of wood were conducted for improving either its dimensional stability or its biological resistance (Matsuda, 1996). Wood is made up primarily of cellulose, hemicellulose and lignin. Originally, chemical modification of wood was a chemical reaction between some reactive parts of wood components and a simple chemical reagent to form a covalent bond between both wood and chemical (Rowell, 1975; Larsson, 1998). Hydroxyl groups in the wood polymers (i.e. cellulose, hemicellulose and lignin) are the most reactive sites in wood. They are also responsible for the dimensional instability through their hydrogen bonding with water. Chemical modification of wood by reaction of the hydroxyl groups in wood with a chemical reagent is substituting the hydroxyl groups with a stable, covalently bonded, less hydrophilic group, which leads to an increased dimensional stability (Larsson, 1998).

In order to chemical modification of wood, many chemicals capable of forming covalent bonds have been studied. The created bond between the wood polymers and the reagent is of great importance to make a permanent modification in wood. The major important types of covalent bonds formed by chemical modification of wood are ethers, esters and acetals (Matsuda, 1996; Larsson, 1998). Studies on chemical modification have been extensively reviewed over the last decades (e.g. Dreher *et al.*, 1964; Rowell, 1975; Rowell, 1982; Rowell *et al.*, 1994) and are more recently, this area has been reviewed by several authors (Kumar, 1994; Beckers & Militz, 1994; Militz & Beckers, 1994a; Beckers *et al.*, 1995; Matsuda, 1996; Militz *et al.*, 1997; Beckers *et al.*, 1998; Rowell *et al.*, 1998; Larsson, 1998; Larsson, 1999 a&b; Gomez-Bueso *et al.*, 1999 a&b; Hill *et al.*, 2000; Chang *et al.*, 2000; Pan & Sano, 2000; Rosenqvist, 2001; Sander & Koch, 2001; Li *et al.*, 2001).

Chemical modification of wood improves its properties by altering the basic molecular structure of cell wall components. It implies the combination of two very different expertise, wood chemistry and wood anatomy. Thus, chemical modification of wood is very complex and requires a multidisciplinary approach. In many chemical modification of wood, reactions of hydroxyl groups play main leading role. In this case wood reacts as an alcohol. Many chemicals have been used to modify wood. The main reaction types are:

### 1.2.1. Etherification

Etherification of wood can be conducted by reacting wood with alkyl halides, acrylonitrile (AN), epoxides,  $\beta$ -propiolactone (acid conditions) and dimethyl sulfate (Matsuda, 1996). During the etherification the hydrogen within the hydroxyl group of a cell wall polymer is substituted by an alkyl group (fig. 1-1).

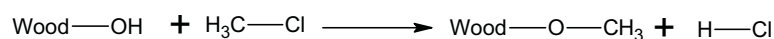


**Fig. 1-1.** Etherification of wood

The formation of an ether bond can be the result of an alkylation or epoxidation of the wood.

#### a. Alkylation

In the reaction of alkyl chlorides with wood, hydrochloric acid is formed as a by-product. Because of this, a great deal of wood degradation takes place during the reaction (Rowell & Banks, 1982). The simplest ether is formed during methylation of wood. This can be achieved by reaction with methylchloride (fig. 1-2).

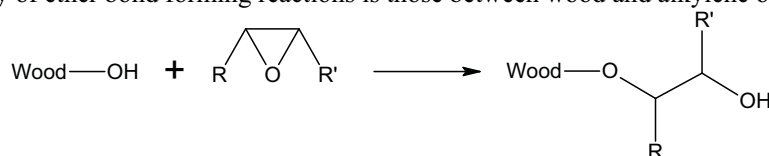


**Fig. 1-2.** Etherification of wood using methylchloride

Another methylation has been achieved by a treatment of wood with dimethyl sulfate or methyl iodide (Militz *et al.*, 1997). Methylated wood though is mechanically impaired because of severe reaction conditions (Kumar, 1994) and the by-product formed. This alkylation of wood gives a high initial antishrink efficiency (ASE) but the effects of the alkylation are lost over time (Militz *et al.*, 1997). In case of reaction of wood with an alkyl chloride in pyridine, the ASE is not caused by the formation of an ether bond with holocellulose or lignin but by the formation of alkyl pyridinium chloride polymers which have the effect of bulking, but are easily leached out (Rowell & Banks, 1982).

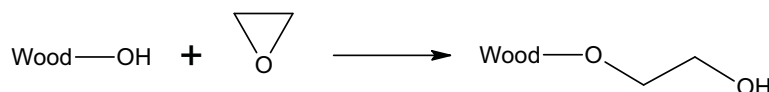
#### b. Epoxidation

Another category of ether bond forming reactions is those between wood and alkylene oxides (fig. 1-3).



**Fig. 1-3.** Reaction of wood with an epoxide

The reaction of wood with epoxides is an example of a polymerizing addition. The used chemical reacts initially with a wood cell wall hydroxyl group and subsequently polymerizes by addition to the new formed hydroxyl group which arises from the epoxide. Several epoxides have been used the past decades for wood modification purposes. They include ethylene oxide (EO), propylene oxide (PO) and butylenes oxide (BO) (Norimoto *et al.*, 1992; Militz *et al.*, 1997; Rowell & Ellis, 1984; Akitsu *et al.*, 1993) and epichlorohydrin (EpCl) (Matsuda, 1993; Goethals & Stevens, 1994). The stability of the treated product and the effects generated vary with the reactant and method of treatment. Epoxidation takes place at elevated temperature and pressure. Usually the reaction is catalyzed under mildly basic conditions. In most experiments triethylamine (TEA) is used as a catalyst (figs. 1-4 & 1-5).



**Fig. 1-4.** Reaction of wood with ethylene oxide (EO)

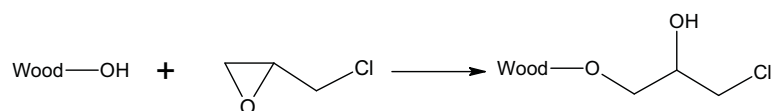


Fig. 1-5. Reaction of wood with epichlorohydrin (EpCl)

### c. Benzylation

Benzylation has been carried out with wood meal to convert wood to thermoplastic materials. Different parameters were used for obtaining benzylated woods with different degrees of substitution. Results showed that pretreatment of the wood with NaOH as a swelling agent and water as a solvating agent, as well as varying reaction temperatures, had critical effects on the benzylation reaction. The reaction proceeds by the following mechanism (Matsuda, 1996; Hiraoka *et al.*, 1997) (fig.1-6 ).

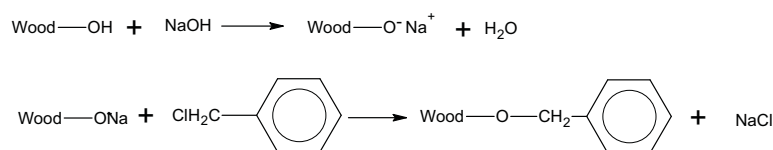


Fig. 1-6. Benzylation of wood with benzylchloride

### d. Allylation

In this case, wood meal is pretreated with a NaOH aqueous solution and reacted with allyl chloride or allyl bromide (fig 1-7). It was found that allyl bromide gave better results than allyl chloride (Matsuda, 1996).

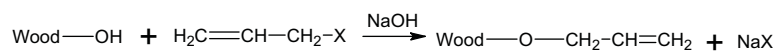


Fig. 1-7. Allylation of wood with an allyl halogen

### e. Cyanoethylation

Reaction of wood with acrylonitrile (AN) produces cyanoethylated wood (Matsuda, 1996). In this case, before any reaction, wood is pretreated with NaOH aqueous solution and the degree of reaction is generally low (fig. 1-8).



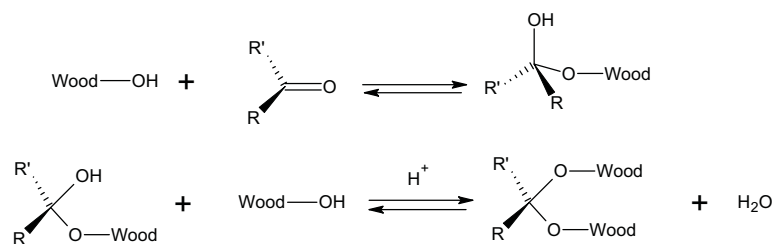
Fig. 1-8. Cyanoethylation of wood with ethylene cyanide

### f. Acetals

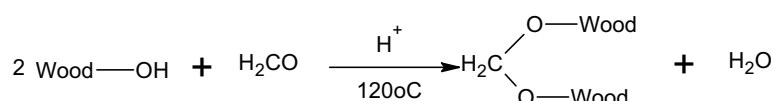
A half acetal is formed by adding a carbonyl group of a modifying agent (aldehyde or kenton) to an alcohol (hydroxyl group of the wood cell wall polymers). This half acetal can further react with a second hydroxyl group of the cell wall polymers (cross-linking) and an acetal bond is formed (fig. 1-9). Several acids have been used as catalysts as well as sulfur dioxide (SO<sub>2</sub>) (Akitsu *et al.*, 1993).

One of the aldehydes, which is used and reported most frequently in literatures, is formaldehyde. This treatment was first reported by Tarkow and Stamm at 1953 (Matsuda, 1996). Akitsu *et al.* (1993) used sulfurdioxide as catalyst. Yano & Minato (1993) and Yasuda & Minato (1994) treated wood samples using formaldehyde and SO<sub>2</sub> at 120°C for 24 hours (fig. 1-10).

## Biological attack of acetylated wood



**Fig. 1-9.** Acetalation of wood

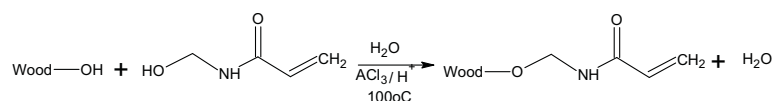


**Fig. 1-10.** Reaction of wood with formaldehyde

Besides formaldehyde other cross-linking chemicals have also been used. They include glyoxal, glutaraldehyde and dimethylol dihydroxyethylene urea (DMDHEU). Treatment with these reagents was carried out with  $\text{SO}_2$ , being an excellent catalyst for acetalation, by Yasuda & Minato (1994) and Yusuf *et al.* (1994, 1995). Reactions were carried out at  $120^\circ\text{C}$  for 24 hours. The concentration used from 5 to 25% in water for glyoxal and glutaraldehyde. Other catalysts which have been used with DMDHEU are aluminum chloride, citric and tartaric acid. Treatments were carried out with aqueous solutions of 10-95% at temperatures of  $80\text{--}175^\circ\text{C}$  (Militz, 1993).

### g. Aminals

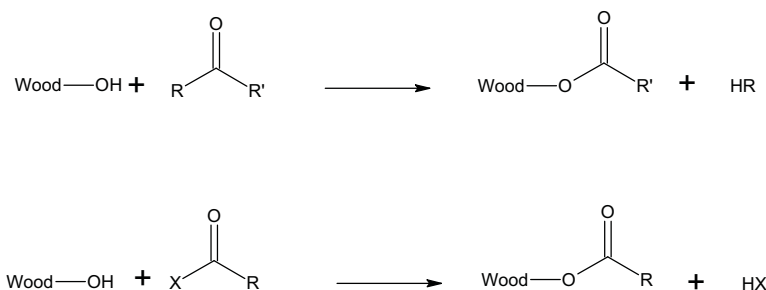
As a special case of ether formation, the reaction between wood and N-hydroxymethylacrylamide (NHMA) could be mentioned (Goethals & Stevens, 1994) (fig. 1-11).



**Fig. 1-11.** Reaction of wood with N-hydroxymethylacrylamide (NHMA)

### 1.2.2. Esterification

Esters are formed by reaction of wood with carboxylic acids or acid anhydrides (fig. 1-12). Ester bonds are liable to acid or base attack, which leads to hydrolysis.



**Fig. 1-12.** Esterification of wood; R: Alkyl group or proton (H) , X: Halogen